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Extended superstructure in Tl-rich liquid Cs–Tl alloys

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The structure factors of liquid caesium–thallium alloys with thallium concentrations of 50 to 85 at. % have been measured by means of neutron diffraction. They exhibit a prepeak which shifts to smaller wave vectors with increasing thallium content. This result is explained using a model in which neutral units Cs_mTl_n are dissolved in an excess of liquid thallium. © *1998 American Institute of Physics.* [S0021-9606(98)70122-3]

INTRODUCTION

Long-range superstructures, characterized by a prepeak in the structure factor at small wave vectors, have been reported previously in liquid K–Tl and Cs–Tl alloys.[1,2] The superstructures were attributed to the occurrence of large Tl clusters in the liquid. The clusters are supposed to be remnants of Tl_{11} or Tl_6 polyanions found in crystalline alloys of the kind A_8B_{11} and A_6B_6 (A=K, Rb, Cs; B=In, Tl) by various authors.[3–8] The periodicity of the superstructure in the different liquid materials is about 10 Å and is quite close to the intercluster distance in the corresponding crystalline compounds. It was first believed[1] that Tl_{11} clusters occurred in liquid KTl, later a number of 8–9 atoms per cluster was preferred.[9] The corresponding solid alloys take a position in between intermetallic and ionic compounds are often characterized as Zintl compounds.[10] They crystallize in a variety of fascinating structures, which are described in a recent review.[11] Covalent bonding between anions is a common phenomenon. The bonding properties are described in terms of electron counting rules given by Pearson[12] and by Wade.[13] A review of liquid Zintl compounds is given in Ref. 9.

The measurements on liquid alkali-group-13 alloys presented in Refs. 1 and 2 were mostly confined to compositions around 50%. As the superstructure is extremely long ranged for a liquid alloy, it was decided to carry out further neutron diffraction studies of these systems. As the alkali metal we chose caesium rather than potassium, because caesium alloys are expected to be more stable.[9]

Thallium was the obvious polyvalent component as indium suffers from a too strong neutron absorption. Finally, the measurements were restricted to the thallium-rich part of the composition range because a low stability is expected in the alkali-rich systems and because the high neutron absorption by caesium would become troublesome.

Measurements of the pressure and temperature dependence of the structure of liquid CsTl were reported by the Dortmund group.[14] The influence of doping liquid KTl with palladium was discussed in Ref. 15.

EXPERIMENT

We measured the structure of five liquid Cs–Tl alloys with thallium content ranging from 50 to 85 at. % (see Table I). The Studsvik Liquids and Amorphous materials Diffractometer SLAD was used and the data were fully corrected for experimental effects using the Studsvik software package CORRECT.[16] The results for $\langle b\rangle^2\{S(k)-1\}$ are given in Fig. 1 for all five alloys. $S(k)$ is the total structure factor, k is the wave vector, and $\langle b\rangle$ the average coherent scattering length of the alloy. There is a well-defined prepeak to the left of the main peak at remarkably low k, which shifts toward smaller k with increasing Tl content, whereas the main peak shifts toward higher k values. The positions of the prepeaks are given in Table I.

INTERPRETATION

The most conspicuous feature of the data is the gradual shift with increasing Tl content of the prepeak position toward lower wave numbers. For analyzing this feature we use as rules of thumb some crude relationships given in Ref. 9. It was shown that even though the polyanions are not completely intact in the liquid, the assumption of perfect polyanions leads to very satisfactory results for most of the basic properties.

Consider as an example Cs_8Tl_{11}. The crystallographic unit cell contains six equivalent formula units, each consisting of a central polyhedron Tl_{11}, surrounded by eight Cs atoms. The precise allocation of a caesium atom to either of two neighboring polyhedra is not essential for our discussion. In the following we denote the Tl_{11} polyhedron by the term ''cluster,'' the augmented polyhedron Cs_8Tl_{11} by the term ''unit.'' The volume of the unit, Ω_{unit}, is equal to the total volume V of the sample divided by the total number of units. Ω_{unit} corresponds to Ω in Ref. 9, where it was defined as V divided by the number of clusters. It is trivial to generalize these definitions to an arbitrary unit A_mB_n. We introduce furthermore $\omega=\Omega_{\text{unit}}/n$, the total volume divided by the number of single anions. If k_0 is the wave vector at which a prepeak is found and d an average intercluster distance (measured between the centers of the clusters), we found in Ref. 9

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TABLE I. In the columns from left to right: The experimentally determined prepeak position k_0, the corresponding periodicity d in real space [Eq. (1)], the average atomic volume Ω_0 of the alloy interpolated from crystallographic data, n is the number of B atoms (Tl) in Ω_{unit} according to Eq. (3) and m is the number of A atoms (Cs) in Ω_{cell} according to Eq. (7). The values of n and m decrease an arbitrary 12% if the volume expansion during melting is taken into account.

Composition	k_0 /Å^{-1}(exp)	d/Å	Ω_0 /Å^3	n [Eq. (3)]	m [Eq. (7)]
CsTl	0.74±0.005	10.40±0.07	46.8	8.5±0.2	8.5±0.2
Cs_8Tl_{11}	0.73±0.005	10.55±0.07	43.9	11.0±0.2	8.0±0.2
$CsTl_2$	0.70±0.005	11.00±0.08	40.7	15.4±0.3	7.7±0.2
$CsTl_3$	0.66±0.005	11.66±0.09	37.7	22.3±0.5	7.5±0.2
$Cs_{15}Tl_{85}$	0.62±0.01	12.42±0.2	34.1	33.8±1.6	6.0±0.3

$$k_0 d = 7.7 \tag{1}$$

and

$$d = 2^{1/6}(\Omega_{\text{unit}})^{1/3}. \tag{2}$$

Equation (2) is based on a model in which the units are put on an fcc lattice. This formula can be used to find an effective average intercluster distance in a crystal, when not all intercluster distances in the ''first coordination shell'' are equal, as well as in a liquid.

Finally, Eq. (2) can be rewritten as

$$n = d^3/(\omega\sqrt{2}). \tag{3}$$

According to Eq. (1) the observed change of the prepeak position with increasing thallium content corresponds to increasing intercluster distances. In Refs. 1 and 9 the analysis was based on the occurrence of complete A_8Tl_{11} or A_6Tl_6 units in the liquid. This leads to satisfactory results even though it is probable that some dissociation and deformation takes place in the liquid.

The question arises which geometrical units develop in the more thallium-rich alloys. If one supposes that, in first approximation, the whole liquid is made up of large, well-defined units, the size of the units, more particularly the number of thallium atoms, would become very large. A calculation according to Eq. (3) shows that in $Cs_{15}Tl_{85}$ n would be approximately 30 (Table I). Scanning the crystallographic literature on the alkali-group-13 compounds one finds that such large configurations are very rare.[11] Particularly stable configurations are B_{11} (capped trigonal prisms), B_{12} (icosahedra), B_{13} and some configurations with $n<11$. Larger polyanions sometimes occur but only when they can be accommodated by ''size tuning.'' The stability of such large units in the liquid is therefore doubtful, and we propose another model: that of well-defined geometrical units, not dissimilar to molecules, dissolved in liquid thallium. The obvious candidates for such units, called central units below, are then Cs_6Tl_6 and Cs_8Tl_{11}.

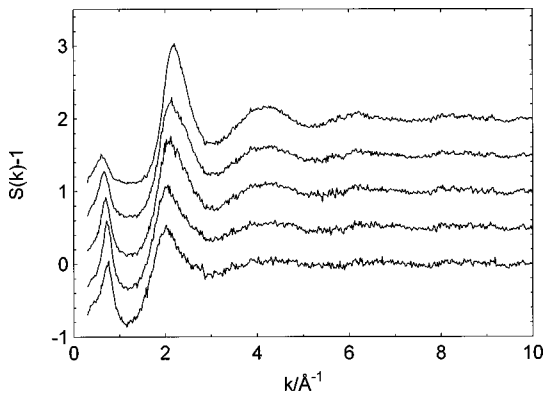

FIG. 1. The measured structure factors of liquid Cs–Tl. From bottom to top: CsTl, Cs_8Tl_{11}, $CsTl_2$, $CsTl_3$, and $Cs_{15}Tl_{85}$, with vertical shifts of 0, 0.5, 1, 1.5, and 2, respectively.

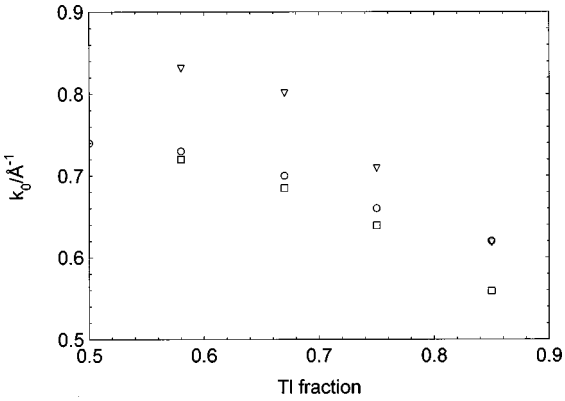

FIG. 2. The prepeak position in liquid Cs–Tl as a function of the Tl concentration. Circles: experimentally determined; squares: calculated according to a model with Cs_8Tl_{11} units; triangles: calculated according to a model with Cs_6Tl_6 units.

The prepeak position is calculated in the following way. Let the central unit be A_mB_n and the composition of the liquid be given by A_xB_y. Write the latter as $A_mB_{my/x} = A_mB_nB_{((my/x)-n)}$, where $(my/x)-n$ is the number of ''solvent'' atoms (anions) surrounding a central unit A_mB_n. We call this conglomerate of central unit+associated solvent atoms the cluster cell. Its volume, Ω_{cell}, is taken equal to the sum of Ω_{unit}, the volume of the central unit, and $((my/x)-n)\Omega_B$, where $\Omega_B=$ is the atomic volume of pure, metallic B. Here two approximations will be made. First, Ω_{unit} is taken from crystallographic data and consequently is smaller than its average value in the liquid. Second, the solvent B is not purely metallic, but its charge is small and negative: only a little extra charge is added to a shell already containing three electrons. Thus according to Eq. (2),

$$d = 2^{1/6}\Omega_{\text{cell}}^{1/3}, \tag{4}$$

with

$$\Omega_{\text{cell}} = \Omega_{\text{unit}} + ((my/x)-n)\Omega_B. \tag{5}$$

The wave vector k_0 is then calculated with Eqs. (1) and (2), with Ω_{unit} in Eq. (2) replaced by Ω_{cell}. The following numbers were used: $\Omega_B=28.6$ Å^3 for thallium. Furthermore, $\Omega_{\text{unit}}=864.3$ and 561.8 Å^3 for Cs_8Tl_{11} and Cs_6Tl_6, respectively, according to Refs. 3 and 8.

The results are plotted in Fig. 2 and tabulated in Table II. Obviously if Cs_8Tl_{11} is taken as central unit, the agreement is excellent except for the alloy with 85% Tl. In the latter case Cs_6Tl_6 is a more satisfactory choice. In both cases the general trend is reproduced very well. In view of the crude ap-

TABLE II. The prepeak position calculated by models using Cs_8Tl_{11} and Cs_6Tl_6, respectively, as a central unit, compared to the experimentally determined values. The values of k_0 decrease ~4% if the volume expansion during melting is taken into account.

		Central units Cs_8Tl_{11}		Central units Cs_6Tl_6	
Composition	k_0 /Å^{-1} (exp)	Ω_{cell} /Å^3	k_0 /Å^{-1} (calc)	Ω_{cell} /Å^3	k_0 /Å^{-1} (calc)
CsTl	0.74±0.005	···	···	562	0.832
Cs_8Tl_{11}	0.73±0.005	864	0.72	626	0.802
$CsTl_2$	0.70±0.005	1007	0.685	733	0.761
$CsTl_3$	0.66±0.005	1236	0.639	905	0.710
$Cs_{15}Tl_{85}$	0.62±0.005	1846	0.559	1363	0.619

proximations made the quantitative agreement may be somewhat fortuitous. It would be easy to generalize Eq. (5) to a system containing both Tl_6 and Tl_{11} clusters. Exact agreement with experiment could then be obtained, but the physical meaning of such an exercise is questionable.

This picture is still based on the fiction of perfect units A_mB_n. It can be generalized to a model in which only one basic property, the number of cations in a cluster cell, m, figures and which is independent of any precise assumptions about the cluster configuration. Treating this time the Tl atoms bound in a cluster and free, ''metallic'' Tl atoms on equal footing, we write the composition of a cluster cell as $A_mB_{my/x}$. k_0 can then be calculated from the mean atomic volume, Ω_0 (the average over all atoms of both kinds). Ω_0 can be obtained by interpolation of the known unit cell volumes of the solid alloys CsTl, Cs_8Tl_{11}, $Cs_{15}Tl_{27}$, and pure thallium (see below). The volume of the cluster cell is then

$$\Omega_{cell} = m(1+y/x)\Omega_0, \tag{6}$$

from which k_0 can be calculated as before. The differences with the results obtained by the first method are insignificant and the new values of k_0 are therefore not listed. This agreement justifies our approach of treating all Tl atoms on equal footing. The value of k_0 obtained in this way is related to m by

$$m = (7.7)^3/((1+y/x)\Omega_0 k_0^3\sqrt{2}), \tag{7}$$

and m can be calculated from the experimental values of k_0. When m is calculated this way it is simply the number of cations in the cell. As we no longer make the difference between anions within and outside the cluster, and probably neutron diffraction cannot distinguish between them either, the periodicity corresponding to the observed prepeak can be best ascribed to the distribution of cations. This implies that the cations are not distributed homogeneously but are grouped together in some way or another, probably in configurations similar to the units found in the crystals.

The values of m are included in Table I. They show a gradual decrease with thallium concentration with a jump downward between 75% and 85% thallium. It is remarkable that m is fairly constant over the Tl concentration range from 50% to 75%.

In our calculations we have used densities derived from crystallographic data, as values for the liquid compounds are not known. For a rough estimate of the error made in this way, we consider two related ionic alloy systems for which liquid densities have been measured, viz. KPb and KTl. Densities of liquid KPb have been reported in Refs. 17–19, while the volume of the unit cell was reported in Ref. 20. The volume expansion due to heating and melting turns out to be approximately 17%. Likewise we find by comparison of data in Refs. 21 and 3, 22, 23 that the volume expansion is approximately 13% for KTl, 5.5% for K_8Tl_{11} and 11% for $K_{49}Tl_{108}$. The atomic volumes of all the solid compounds of composition A_8Tl_{11} are relatively high, which explains the low expansion found. In case of the Cs–Tl alloys the mean atomic volumes of solid CsTl,[8] $Cs_{15}Tl_{27}$,[24] and pure Tl, when plotted as a function of composition, fit almost precisely to a straight line, whereas the value for Cs_8Tl_{11}[3] is too high by 3.3%. In our calculations we have used the values corresponding to the straight line.

Correcting the atomic volumes upward by an arbitrary 12% for volume expansion during heating and melting would result in a change downward of the calculated values of k_0 in Table II and Fig. 2 by only 4%. The values of n and m, however, are proportional to the volume and are therefore more seriously affected. Our analysis hinges on the use of the formulas (1)–(3). But their validity as empirical rules has been confirmed for a wide range of compounds.[9]

The present interpretation is based on prepeak positions only. A detailed analysis of the structure factor beyond the prepeak may provide more information on the distribution of cluster sizes and the shape of the clusters. This analysis is in progress.

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